

DRAFT PERFORMANCE SPECIFICATION 12 -- Specifications and test procedures for total mercury continuous monitoring systems in stationary sources

1. *Applicability and Principle*

1.1 Applicability. This specification is to be used for evaluating the acceptability of total mercury continuous emission monitoring systems (CEMS) at the time of or soon after installation and whenever specified in the regulations. The CEMS must be capable of measuring the total concentration (regardless of speciation) of both vapor and solid phase mercury. The CEMS may include, for certain stationary sources, a) a diluent (O<sub>2</sub>) monitor (which must meet its own performance specifications: 40 CFR part 60, Appendix B, Performance Specification 3), b) flow monitoring equipment to allow measurement of the dry volume of stack effluent sampled, and c) an automatic sampling system.

This specification is not designed to evaluate the installed CEMS' performance over an extended period of time nor does it identify specific calibration techniques and auxiliary procedures to assess the CEMS' performance. The source owner or operator, however, is responsible to properly calibrate, maintain, and operate the CEMS. To evaluate the CEMS' performance, the Administrator may require, under Section 114 of the Act, the operator to conduct CEMS performance evaluations at other times besides the initial test.

1.2 Principle. Installation and measurement location

specifications, performance specifications, test procedures, and data reduction procedures are included in this specification. Reference method tests, calibration error tests, and calibration drift tests, and interferant tests are conducted to determine conformance of the CEMS with the specification. Calibration error is assessed with standards for elemental mercury ( $\text{Hg}(0)$ ) and mercuric chloride ( $\text{HgCl}_2$ ). The ability of the CEMS to provide a measure of total mercury (regardless of speciation and phase) at the facility at which it is installed is demonstrated by comparison to manual reference method measurements.

## *2. Definitions*

2.1 Continuous Emission Monitoring System (CEMS). The total equipment required for the determination of a pollutant concentration. The system consists of the following major subsystems:

2.1.1 Sample Interface. That portion of the CEMS used for one or more of the following: sample acquisition, sample transport, and sample conditioning, or protection of the monitor from the effects of the stack effluent.

2.1.2 Pollutant Analyzer. That portion of the CEMS that senses the pollutant concentration(s) and generates a proportional output.

2.1.3 Diluent Analyzer (if applicable). That portion of the CEMS that senses the diluent gas ( $\text{O}_2$ ) and generates an output proportional to the gas concentration.

2.1.4 Data Recorder. That portion of the CEMS that provides a permanent record of the analyzer output. The data recorder may provide automatic data reduction and CEMS control capabilities.

2.2 Point CEMS. A CEMS that measures the pollutant concentrations either at a single point or along a path equal to or less than 10 percent of the equivalent diameter of the stack or duct cross section.

2.3 Path CEMS. A CEMS that measures the pollutant concentrations along a path greater than 10 percent of the equivalent diameter of the stack or duct cross section.

2.4 Span Value. The upper limit of a pollutant concentration measurement range defined as twenty times the applicable emission limit. The span value shall be documented by the CEMS manufacturer with laboratory data.

2.5 Relative Accuracy (RA). The absolute mean difference between the pollutant concentration(s) determined by the CEMS and the value determined by the reference method (RM) plus the 2.5 percent error confidence coefficient of a series of tests divided by the mean of the RM tests or the applicable emission limit.

2.6 Calibration Drift (CD). The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.7 Zero Drift (ZD). The difference in the CEMS output readings for zero input after a stated period of operation during

which no unscheduled maintenance, repair, or adjustment took place.

2.8 Representative Results. Defined by the RA test procedure defined in this specification.

2.9 Response Time. The time interval between the start of a step change in the system input and the time when the pollutant analyzer output reaches 95 percent of the final value.

2.10 Centroidal Area. A concentric area that is geometrically similar to the stack or duct cross section and is no greater than 1 percent of the stack or duct cross sectional area.

2.11 Batch Sampling. Batch sampling refers to the technique of sampling the stack effluent continuously and concentrating the pollutant in some capture medium. Analysis is performed periodically after sufficient time has elapsed to concentrate the pollutant to levels detectable by the analyzer.

2.12 Calibration Standard. Calibration standards consist of a known amount of pollutant that is presented to the pollutant analyzer portion of the CEMS in order to calibrate the drift or response of the analyzer. The calibration standard may be, for example, a solution containing a known concentration, or a filter with a known mass loading or composition.

2.13 Calibration Error (CE). The difference between the concentration indicated by the CEMS and the known concentration generated by a calibration source when the entire CEMS, including the sampling interface) is challenged. A CE test procedure is performed to document the accuracy and linearity of the CEMS over

the entire measurement range.

### *3. Installation and Measurement Location Specifications*

3.1 The CEMS Installation and measurement location. Install the CEMS at an accessible location downstream of all pollution control equipment where the mercury concentration measurements are directly representative or can be corrected so as to be representative of the total emissions from the affected facility. Then select representative measurement points or paths for monitoring in locations that the CEMS will pass the RA test (see Section 7). If the cause of failure to meet the RA test is determined to be the measurement location and a satisfactory correction technique cannot be established, the Administrator may require the CEMS to be relocated.

Measurement locations and points or paths that are most likely to provide data that will meet the RA requirements are listed below.

3.1.1 Measurement Location. The measurement location should be (1) at least eight equivalent diameters downstream of the nearest control device, point of pollutant generation, bend, or other point at which a change of pollutant concentration or flow disturbance may occur and (2) at least two equivalent diameters upstream from the effluent exhaust. The equivalent duct diameter is calculated as per 40 CFR part 60, Appendix A, Method 1, Section 2.1.

3.1.2 Point CEMS. The measurement point should be (1) no

less than 1.0 meter from the stack or duct wall or (2) within or centrally located over the centroidal area of the stack or duct cross section. Selection of traverse points to determine the representativeness of the measurement location should be made according to 40 CFR part 60, Appendix A, Method 1, Section 2.2 and 2.3.

3.1.3 Path CEMS. The effective measurement path should be (1) totally within the inner area bounded by a line 1.0 meter from the stack or duct wall, or (2) have at least 70 percent of the path within the inner 50 percent of the stack or duct cross sectional area, or (3) be centrally located over any part of the centroidal area.

3.2 Reference Method (RM) Measurement Location and Traverse Points. The RM measurement location should be (1) at least eight equivalent diameters downstream of the nearest control device, point of pollutant generation, bend, or other point at which a change of pollutant concentration or flow disturbance may occur and (2) at least two equivalent diameters upstream from the effluent exhaust. The RM and CEMS locations need not be the same, however the difference may contribute to failure of the CEMS to pass the RA test, thus they should be as close as possible without causing interference with one another. The equivalent duct diameter is calculated as per 40 CFR part 60, Appendix A, Method 1, Section 2.1. Selection of traverse measurement point locations should be made according to 40 CFR part 60, Appendix A, Method 1, Sections

2.2 and 2.3. If the RM traverse line interferes with or is interfered by the CEMS measurements, the line may be displaced up to 30 cm (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area.

#### 4. *Performance and Equipment Specifications*

4.1 Data Recorder Scale. The CEMS data recorder response range must include zero and a high level value. The high level value must be equal to the span value. If a lower high level value is used, the CEMS must have the capability of providing multiple outputs with different high level values (one of which is equal to the span value) or be capable of automatically changing the high level value as required (up to the span value) such that the measured value does not exceed 95 percent of the high level value.

4.2 Relative Accuracy (RA). The RA of the CEMS must be no greater than 20 percent of the mean value of the RM test data in terms of units of the emission standard, or 10 percent of the applicable standard, whichever is greater.

4.3 Calibration Error. Calibration error is assessed using standards for Hg(0) and HgCl<sub>2</sub>. The mean difference between the indicated CEMS concentration and the reference concentration value for each standard at all three test levels listed below shall be no greater than  $\pm 15$  percent of the reference concentration at each level.

4.3.1 Zero Level. Zero to twenty (0 - 20) percent of the emission limit.

4.3.2 Mid-Level. Forty to sixty (40 - 60) percent of the emission limit.

4.3.3 High-Level. Eighty to one-hundred and twenty (80 - 120) percent of the emission limit.

4.4 Calibration Drift. The CEMS design must allow the determination of calibration drift of the pollutant analyzer at concentration levels commensurate with the applicable emission standard. The CEMS calibration may not drift or deviate from the reference value (RV) of the calibration standard by more than 10 percent of the emission limit. The calibration shall be performed at a level equal to 80 to 120 percent of the applicable emission standard. Calibration drift shall be evaluated for elemental mercury only.

4.5 Zero Drift. The CEMS design must allow the determination of calibration drift at the zero level (zero drift). The CEMS zero point shall not drift by more than 5 percent of the emission standard.

4.6 Sampling and Response Time. The CEMS shall sample the stack effluent continuously. Averaging time, the number of measurements in an average, and the averaging procedure for reporting and determining compliance shall conform with that specified in the applicable emission regulation.

4.6.1 Response Time. The response time of the CEMS should not exceed 2 minutes to achieve 95 percent of the final stable value. The response time shall be documented by the CEMS



manufacturer.

4.6.2 Waiver from Response Time Requirement. A source owner or operator may receive a waiver from the response time requirement for instantaneous, continuous CEMS in section 4.5.1 from the Agency if no CEM is available which can meet this specification at the time of purchase of the CEMS.

4.6.3 Response Time for Batch CEMS. The response time requirement of Section 4.5.1 does not apply to batch CEMS. Instead it is required that the sampling time be no longer than one third of the averaging period for the applicable standard. In addition, the delay between the end of the sampling time and reporting of the sample analysis shall be no greater than one hour. Sampling is also required to be continuous except in that the pause in sampling when the sample collection media are changed should be no greater than five percent of the averaging period or five minutes, whichever is less.

4.7 CEMS Interference Response. While the CEMS is measuring the concentration of mercury in the high-level calibration sources used to conduct the CE test the gaseous components (in nitrogen) listed in Table I shall be introduced into the measurement system either separately or in combination. The interference test gases must be introduced in such a way as to cause no change in the mercury or mercuric chloride calibration concentration being delivered to the CEMS. The concentrations listed in the table are the target levels at the sampling interface of the CEMS based on

the known cylinder gas concentrations and the extent of dilution (see Section 9). Interference is defined as the difference between the CEMS response with these components present and absent. The sum of the interferences must be less than 10 percent of the emission limit value. If this level of interference is exceeded, then corrective action to eliminate the interference(s) must be taken.

**Table I**  
Interference Test Gas Concentrations in Nitrogen

Gas	Concentration
Carbon Monoxide	500 ± 50 ppm
Carbon Dioxide	10 ± 1 percent
Oxygen	20.9 ± 1 percent
Sulfur Dioxide	500 ± 50 ppm
Nitrogen Dioxide	250 ± 25 ppm
Water Vapor	25 ± 5 percent
Hydrogen Chloride (HCl)	50 ± 5 ppm
Chlorine (Cl <sub>2</sub> )	10 ± 1 ppm

4.8 Calibration Source Requirements for Assessment of Calibration Error. The calibration source must permit the introduction of known (NIST traceable) and repeatable concentrations of elemental mercury (Hg(0)) and mercuric chloride (HgCl<sub>2</sub>) into the sampling system of the CEMS. The CEMS manufacturer shall document the performance of the calibration source, and submit this documentation and a calibration protocol to the administrator for approval. Determination of CEMS calibration error must then be made in using the approved calibration source and in accordance with the approved protocol.

4.8.1 Design Considerations. The calibration source must be designed so that the flowrate of calibration gas introduced to the CEMS is the same at all three calibration levels specified in Section 4.3 and at all times exceeds the flow requirements of the CEMS.

4.8.2 Calibration Precision. A series of three injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than  $\pm 5$  percent from the mean of the three injections. Failure to attain this level of precision is an indication of a problem in the calibration system or the CEMS. Any such problem must be identified and corrected before proceeding.

#### 5. *Performance Specification Test Procedure*

5.1 Pretest Preparation. Install the CEMS and prepare the RM test site according to the specifications in Section 3, and prepare the CEMS for operation according to the manufacturer's written instructions.

5.2 Calibration and Zero Drift Test Period. While the affected facility is operating at more than 50 percent of normal load, or as specified in an applicable subpart, determine the magnitude of the calibration drift (CD) and zero drift (ZD) once each day (at 24-hour intervals) for 7 consecutive days according to the procedure given in Section 6. To meet the requirements of Sections 4.4 and 4.5 none of the CD's or ZD's may exceed the specification. All CD determinations must be made following a 24-hour period during which no unscheduled maintenance, repair, or manual adjustment of the CEMS took place.

5.3 CE Test Period. Conduct a CE test prior to the CD test period. Conduct the CE test according to the procedure given in Section 8.

5.4 CEMS Interference Response Test Period. Conduct an interference response test in conjunction with the CE test according to the procedure given in Section 9.

5.5 RA Test Period. Conduct a RA test following the CD test period. Conduct the RA test according to the procedure given in Section 7 while the affected facility is operating at more than 50 percent of normal load, or as specified in the applicable subpart.

#### 6.0 *The CEMS Calibration and Zero Drift Test Procedure*

This performance specification is designed to allow calibration of the CEMS by use of standard solutions, filters, etc that challenge the pollutant analyzer part of the CEMS (and as much of the whole system as possible), but which do not challenge the entire CEMS, including the sampling interface. Satisfactory response of the entire system is covered by the RA and CE requirements.

The CD measurement is to verify the ability of the CEMS to conform to the established CEMS calibration used for determining the emission concentration. Therefore, if periodic automatic or manual adjustments are made to the CEMS zero and calibration settings, conduct the CD test immediately before the adjustments, or conduct it in such a way that the CD and ZD can be determined.

Conduct the CD and ZD tests at the points specified in Sections 4.4 and 4.5. Record the CEMS response and calculate the CD according to:

$$CD = \frac{(R_{CEM} - R_V)}{R_V} \times 100 , \quad (1)$$

where CD denotes the calibration drift of the CEMS in percent,  $R_{CEM}$  is the CEMS response, and  $R_V$  is the reference value of the high level calibration standard. Calculate the ZD according to:

$$ZD = \frac{(R_{CEM} - R_V)}{R_{EM}} \times 100 , \quad (2)$$

where ZD denotes the zero drift of the CEMS in percent,  $R_{CEM}$  is the CEMS response,  $R_V$  is the reference value of the low level calibration standard, and  $R_{EM}$  is the emission limit value.

## 7. *Relative Accuracy Test Procedure*

7.1 Sampling Strategy for RA Tests. The RA tests are to verify the initial performance of the entire CEMS system, including the sampling interface, by comparison to RM measurements. Conduct the RM measurements in such a way that they will yield results representative of the emissions from the source and can be correlated to the CEMS data. Although it is preferable to conduct the diluent (if applicable), moisture (if needed), and pollutant measurements simultaneously, the diluent and moisture measurements that are taken within a 30- to 60-minute period, which includes the pollutant measurements, may be used to calculate dry pollutant concentration.

A measure of relative accuracy at a single level that is

detectable by both the CEMS and the RM is required.

In order to correlate the CEMS and RM data properly, note the beginning and end of each RM test period of each run (including the exact time of day) in the CEMS data log.

7.2 Correlation of RM and CEMS Data. Correlate the CEMS and RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration for each RM test period. Consider system response time, if important, and confirm that the pair of results are on a consistent moisture, temperature, and diluent concentration basis. Then compare each integrated CEMS value against the corresponding average RM value.

7.3 Number of tests. Obtain a minimum of three pairs of CEMS and RM measurements. If more than nine pairs of measurements are obtained, then up to three pairs of measurements may be rejected so long as the total number of measurement pairs used to determine the RA is greater than or equal to nine. However, all data, including the rejected data, must be reported.

7.4 Reference Methods. Unless otherwise specified in an applicable subpart of the regulations, Method 3B, or its approved alternative, is the reference method for diluent ( $O_2$ ) concentration. Unless otherwise specified in an applicable subpart of the regulations, the manual method for multi-metals in 40 CFR part 266, Appendix IX, Section 3.1 (until superseded by

SW-846), or its approved alternative, is the reference method for mercury.

7.5 Calculations. Summarize the results on a data sheet. An example is shown is shown in Figure 2-2 of 40 CFR part 60, Appendix B, Performance Specification 2. Calculate the mean of the RM values. Calculate the arithmetic differences between the RM and CEMS output sets, and then calculate the mean of the differences. Calculate the standard deviation of each data set and CEMS RA using the equations in Section 10.

## 8. *Calibration Error Test Procedure*

8.1 Sampling Strategy. The CEMS calibration error shall be assessed using calibration sources of elemental mercury and mercuric chloride in turn (see Section 4.8 for calibration source requirements). Challenge the CEMS at the measurement levels specified in Section 4.3. During the test, operate the CEMS as nearly as possible in its normal operating mode. The calibration gases should be injected into the sampling system as close to the sampling probe outlet as practical and shall pass through all filters, scrubbers, conditioners, and other monitor components used during normal sampling.

8.2 Number of tests. Challenge the CEMS three non-consecutive times at each measurement point and record the responses. The duration of each challenge should be for a sufficient period of time to ensure that the CEMS surfaces are conditioned and a stable output obtained.



8.3 Calculations. Summarize the results on a data sheet. Calculate the mean difference between the CEMS response and the known reference concentration at each measurement point according to equations 5 and 6 of Section 10. The calibration error (CE) at each measurement point is then given by:

$$CE = *d/R_v * X100, \quad (3)$$

where  $R_v$  is the reference concentration value.

## 9. *Interference Response Test Procedure*

9.1 Test Strategy. Perform the interference response test while the CEMS is being challenged by the high level calibration source for mercury (after the CE determination has been made), and again while the CEMS is being challenged by the high level calibration source for mercuric chloride (after the CE determination has been made). The interference test gases should be injected into the sampling system as close to the sampling probe outlet as practical and shall pass through all filters, scrubbers, conditioners, and other monitor components used during normal sampling.

9.2 Number of tests. Introduce the interference test gas three times alternately with the high-level calibration gas and record the responses both with and without the interference test gas. The duration of each test should be for a sufficient period of time to ensure that the CEMS surfaces are conditioned and a stable output obtained.

9.3 Calculations. Summarize the results on a data sheet. Calculate the mean difference between the CEMS response with and without the interference test gas by taking the average of the CEMS responses with and without the interference test gas (see equation 5) and then taking the difference (d). The percent interference (I) is then given by:

$$I = *d / R_{HL} * X100 , \quad (4)$$

where  $R_{HL}$  is the value of the high-level calibration standard. If the gaseous components of the interference test gas are introduced separately, then the total interference is the sum of the individual interferences.

## 10. Equations

10.1 Arithmetic Mean. Calculate the arithmetic mean of a data set as follows:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i , \quad (5)$$

where n is equal to the number of data points.

10.1.1 Calculate the arithmetic mean of the difference, d, of a data set, using Equation 5 and substituting d for x. Then

$$d_i = x_i - y_i , \quad (6)$$

where x and y are paired data points from the CEMS and RM, respectively.

10.2 Standard Deviation. Calculate the standard deviation (SD) of a data set as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^n x_i^2 - \frac{1}{n} \left( \sum_{i=1}^n x_i \right)^2}{n - 1}} , \quad (7)$$

10.3 Relative Accuracy (RA). Calculate the RA as follows:

$$RA = \frac{\bar{d} + \frac{t_{0.975}}{\sqrt{n}}(SD)}{\bar{R}_{RM}} , \quad (8)$$

where  $\bar{d}$  is equal to the arithmetic mean of the difference, d,

of the paired CEMS and RM data set, calculated according to Equations 5 and 6, SD is the standard deviation calculated

according to Equation 7,  $\bar{R}_{RM}$  is equal to either the average of

the RM data set, calculated according to Equation 5, or the value of the emission standard, as applicable (see Section 4.2), and  $t_{0.975}$  is the t-value at 2.5 percent error confidence, see Table II.

**TABLE II**  
t-Values

n <sup>a</sup>	t <sub>0.975</sub>	n <sup>a</sup>	t <sub>0.975</sub>	n <sup>a</sup>	t <sub>0.975</sub>
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

<sup>a</sup> The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

#### 11. *Reporting*

At a minimum (check with the appropriate regional office, or State, or local agency for additional requirements, if any) summarize in tabular form the results of the CE, interference response, CD and RA tests. Include all data sheets, calculations, and records of CEMS response necessary to substantiate that the performance of the CEMS met the performance specifications.

The CEMS measurements shall be reported to the agency in units of  $\mu\text{g}/\text{m}^3$  on a dry basis, corrected to 20EC and 7 percent  $\text{O}_2$ .

#### 12. *Bibliography*

1. 40 CFR Part 60, Appendix B, "Performance Specification 2 - Specifications and Test Procedures for  $\text{SO}_2$  and  $\text{NO}_x$  Continuous Emission Monitoring Systems in Stationary Sources."

2. 40 CFR Part 60, Appendix B, "Performance Specification 1 - Specification and Test Procedures for Opacity Continuous

Emission Monitoring Systems in Stationary Sources."

3. 40 CFR Part 60, Appendix A, "Method 1 - Sample and Velocity Traverses for Stationary Sources."

4. 40 CFR Part 266, Appendix IX, Section 2, "Performance Specifications for Continuous Emission Monitoring Systems."

5. Draft Method 29, "Determination of Metals Emissions from Stationary Sources," Docket A-90-45, Item II-B-12, and EMTIC CTM-012.WPF.

6. "Continuous Emission Monitoring Technology Survey for Incinerators, Boilers, and Industrial Furnaces: Final Report for Metals CEM's," prepared for the Office of Solid Waste, U.S. EPA, Contract No. 68-D2-0164 (4/25/94).

7. 40 CFR Part 60, Appendix A, Method 16, "Semicontinuous Determination of Sulfur Emissions from Stationary Sources."

8. 40 CFR Part 266, Appendix IX, Performance Specification 2.2, "Performance Specifications for Continuous Emission Monitoring of Hydrocarbons for Incinerators, Boilers, and Industrial Furnaces Burning Hazardous Waste."